SCIENCE FOR CERAMIC PRODUCTION

COMPOSITE MATERIAL
IN THE ALUMINUM OXIDE – ZIRCONIUM DIOXIDE SYSTEM

N. A. Makarov[1]

A dispersion-hardened material with average flexural strength 580 ± 40 MPa, which is a promising building material, has been fabricated by introducing a $CaO – ZnO – Al_2O_3 – SiO_2$ eutectic additive and tetragonal zirconium dioxide into aluminum oxide synthesized by calcining the hydroxide. The sintering temperature of this ceramic is 1550°C. The properties of the eutectic of this system are analyzed, and the optimal liquid-phase composition which gives intense sintering of the aluminum oxide is determined.

Modern technology requires the development of materials which possess high resistance to forces of different nature: mechanical, chemical, electrophysical, thermal, and others. Undoubtedly, this is true of polymers, ceramics, glass, metal, and composites based on them. Ceramic materials, specifically, aluminum oxide, are best for such purposes.

Aluminum oxide based ceramics have a quite wide range of applications. They can be used in electronics, as thread guides, electric insulators, separators for mixers, wear-resistant milling bodies, and for other purposes. However, the application of such materials is quite limited in areas of technology where large mechanical loads occur (cutting tool, bearings, pump plungers, high-pressure nozzles, and others).

The purpose of the present investigation is to develop a material which is characterized by high physical-mechanical indicators (ultimate flexural strength no lower than 500 MPa) and has sintering temperature 1500 – 1550°C.

Ordinarily, such materials are sintered at temperatures above 1600°C. It has been established that the most promising materials from the standpoint of lowering the sintering temperature are additives of the type $MeO – Al_2O_3 – SiO_2$. The compounds MnO, ZnO, FeO, CaO, and CuO can be used for MeO [1]. Eutectic systems with only one modifying oxide have been investigated in the past (for example, additives where $Me = Mn^{2+}, Fe^{2+}, Cu^{2+}$) [2].

In our work an attempt was made to lower the sintering temperature of corundum ceramic by introducing simultaneously zinc and calcium oxides as the modifying agents.

Calculations performed using Berezhnoi's method show that using these oxides simultaneously gives a melt at 1162°C [3]. Evidently, this will also lower the sintering temperature of the ceramic.

A tetragonal solid solution based on ZrO_2 in a highly dispersed state — partially stabilized zirconium dioxide (PSZD) — was chosen as the component for increasing the mechanical strength.

Thus, an attempt was undertaken to develop an Al_2O_3-based dispersion-hardened composite material containing both a hardening component and a sintering aid (modifier).

The initial materials consisted of the following: GLMK alumina (alloyed with 0.25%[2] MgO); aluminum oxide obtained by calcining commercial aluminum hydroxide (Al_2O_3-H); a eutectic mixture, synthesized by co-precipitation, of aluminum oxide and zirconium dioxide; and, RSZD powder chemically precipitated from zirconium oxychloride in a concentrated solution of ammonia.

The initial mixtures with the computed composition (Table 1) were wet ground and calcined at 1000°C to obtain the sintering additives. The samples ($40 \times 6 \times 4$ mm bars) were produced by bilateral pressing under pressure 100 MPa. The calcination was performed at temperatures 1500, 1550, and 1600°C. The experimental results are presented in Tables 2 and 3.

It should be noted that irrespective of the type of modifying additive, the amount of additive introduced, and the calcination temperature, under otherwise equal conditions, the

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[1] D. I. Mendeleev Russian Chemical Engineering Institute, Moscow, Russia.

[2] Hear and below, unless otherwise state, the mass content.

TABLE 1.

Additive	Mass content, %				DTA melting temperature, °C*
	ZnO	CaO	Al_2O_3	SiO_2	
CZAS-1	37.00	3.10	11.20	48.70	1320
CZAS-2	32.35	10.03	14.31	43.31	1200
CZAS-3	27.91	15.78	17.99	38.32	1250

* The minimum melting temperature calculated by Berezhnoi's method is 1162°C.

water absorption is lower and the mechanical strength is higher for samples based on co-precipitated aluminum and zirconium oxides. This makes sense because of the high sintering activity of the powders synthesized in the most nonequilibrium regime. The ceramic based on Al_2O_3-H, in turn, calcines better than the composites based on GLMK alumina. Hydrostatic pressing increases the average density of the ceramic; this is due to additional densification of the half-finished product during the molding process.

Since adding CZAS-1 to GLMK alumina and Al_2O_3-H does not give a material with high mechanical strength, the properties of the ceramic synthesized on the basis of the eutectic $Al_2O_3 – ZrO_2$ and the indicated additive were not investigated because they are obviously unsatisfactory.

The effect of the additives on the properties of a material, including the sinterability of $Al_2O_3 – ZrO_2$ compositions, is determined by a set of factors, specifically, the melt's acid-base properties, viscosity, and surface tension as well as

other factors. Consequently, for each modifier of the melt it is desirable to analyze the parameters indicated.

The experimental results show that the most and least effective modifiers are CZAS-3 and CZAS-1, respectively. Thus, the Al_2O_3-H based materials containing 3% CZAS-1 as an additive sinter to a dense state only at 1600°C, while compositions with the same amount of the other modifiers do so at 1550°C. The average density and water absorption are very close for all types of modifiers added in the same amounts and for all forms of the initial components. Examining the mechanical properties of the composites shows that the effect of the modifier is stronger in this case. The additives which are most and least effective for increasing the mechanical strength are CZAS-3 and CZAS-1, respectively.

It has been established [1] that the modifier must have the optimal melting temperature, which, as rule, is lowest for silicate melts among all possible melts in each specific system. This is one reason for using additives with eutectic compositions as modifiers.

Berezhnoi's computational method makes it possible to determine only the lowest melting temperature of a system. The thermodynamics function (entropy and enthalpy) and their temperature dependences must be taken into account when using other well-known methods. This leads to quite tedious calculations. Consequently, the melting temperature of the systems was determined by the DTA method (see Table 2). Thus, with respect to obtaining the lowest melting temperature and with respect to the effectiveness of acting on the calcination process the modifiers studied must be ar-

TABLE 2.

Calcination temperature, °C	Average density ρ and water absorption W of the ceramic with modifiers added in the amounts,%																	
	CZAS-1						CZAS-2						CZAS-3					
	3		4		5		3		4		5		3		4		5	
	ρ, g/cm³	W, %	ρ, g/cm³	W, %	ρ, g/cm³	W, %	ρ, g/cm³	W, %	ρ, g/cm³	W, %	ρ, g/cm³	W, %	ρ, g/cm³	W, %	ρ, g/cm³	W, %	ρ, g/cm³	W, %
							GLMK											
1500	3.50	3.50	3.98	0.80	3.90	0.80	3.55	3.00	3.96	0.70	3.98	0.60	3.78	0.31	4.04	0.10	4.00	0.20
1550	3.96	0.20	4.03	0.02	3.96	0.40	4.01	0.10	4.04	0.00	4.02	0.10	4.02	0.07	4.06	0.00	4.05	0.00
1600	4.02	0.02	4.04	0.02	3.98	0.20	4.03	0.00	4.05	0.00	4.03	0.00	4.02	0.00	4.08	0.00	4.05	0.00
							Al_2O_3-H											
1500	3.58	3.00	3.85	1.60	3.90	0.80	3.72	2.5	4.02	0.50	3.97	0.50	3.88	0.30	4.07	0.20	4.04	0.20
1550	3.98	0.20	4.02	0.00	3.96	0.40	4.01	0.00	4.06	0.00	4.05	0.20	4.06	0.02	4.08	0.00	4.06	0.10
1600	4.03	0.00	4.04	0.00	3.98	0.20	4.07	0.00	4.09	0.00	4.07	0.00	4.08	0.00	4.11	0.00	4.08	0.00
							Al_2O_3-H, hydrostatic pressing											
1550	Not determined						4.09	0.00	4.12	0.00	4.10	0.00	4.12	0.00	4.14	0.00	4.12	0.00
							$Al_2O_3 – ZrO_2$											
1500	Not determined						3.97	0.50	4.12	0.00	4.08	0.30	4.00	0.40	4.16	0.00	4.12	0.10
1550	Same						4.14	0.00	4.18	0.00	4.15	0.00	4.16	0.00	4.19	0.00	4.17	0.00
1600	"						4.18	0.00	4.20	0.00	4.17	0.00	4.18	0.00	4.21	0.00	4.19	0.00

TABLE 3.

Calcination temperature, °C	Mechanical strength, MPa, of ceramic with modifiers added in the amounts,%								
	CZAS-1			CZAS-2			CZAS-3		
	3	4	5	3	4	5	3	4	5
	GLMK								
1500	220 ± 20	230 ± 25	220 ± 22	237 ± 21	290 ± 35	230 ± 20	290 ± 32	313 ± 24	280 ± 24
1550	270 ± 23	300 ± 32	260 ± 31	377 ± 34	470 ± 38	340 ± 32	415 ± 36	430 ± 38	380 ± 34
1600	250 ± 18	265 ± 34	210 ± 20	268 ± 35	300 ± 28	210 ± 19	390 ± 27	400 ± 33	360 ± 32
	Al_2O_3-H								
1500	280 ± 25	300 ± 25	280 ± 22	368 ± 32	400 ± 30	318 ± 22	400 ± 25	440 ± 23	390 ± 30
1550	330 ± 30	340 ± 23	320 ± 25	517 ± 38	520 ± 42	400 ± 28	530 ± 40	540 ± 43	430 ± 34
1600	310 ± 32	300 ± 24	270 ± 35	329 ± 25	357 ± 34	310 ± 17	420 ± 25	490 ± 38	400 ± 28
	Al_2O_3-H, hydrostatic pressing								
1550	Not determined			532 ± 42	540 ± 38	460 ± 40	560 ± 42	580 ± 40	500 ± 30
	$Al_2O_3 - ZrO_2$								
1500	Not determined			400 ± 28	430 ± 25	380 ± 32	460 ± 35	500 ± 37	470 ± 35
1550	Same			550 ± 41	580 ± 42	480 ± 34	560 ± 40	600 ± 42	520 ± 37
1600	"			422 ± 30	442 ± 37	410 ± 30	480 ± 32	525 ± 40	480 ± 37

ranged in the following manner: CZAS-2 → CZAS-3 → CZAS-1.

Efficient calcination of aluminum-oxide materials containing low-melting components is possible if the melt is acidic. This is dictated by the fact in that aluminum oxide is amphoteric; the coordination of the Al^{3+} ion depends on the acidity of the melt. In basic media the aluminum ion has a coordination number 4 and is represented by the complexes AlO_4^{5-} and in acidic media its coordination number is 6 and it is represented by the groups AlO_6^{9-}. According to our present understanding, the process becomes intense when the coordination number of aluminum is 6 and the liquid phase is acidic.

Appen's method can be used to assess the acid-base properties of the melt [4]. A measure of the coordination state of aluminum and, therefore, the acidity of the melt in this case is the parameter ψ_{Al} calculated as

$$\psi_{Al} = k\,[MeO]/[Al_2O_3],$$

where [MeO] is the molar fraction of the oxide capable of affecting the coordination state of the aluminum ion — a so-called active oxide — and [Al_2O_3] is the molar fraction of the aluminum oxide in the melt.

There is no generally accepted value of k. A. A. Appen indicates that the ions are those with low charge and large radius, for example, Na^+, K^+, and Ba^{2+}, are most active. In such a case $k = 1$. These ions lower the coordination number of the Al^{3+} ion compared with corundum to 4. The ions Li^+ and Ca^{2+} are less active. The value of k is not presented in this case. Ions with a small radius, for example, Fe^{2+} and Mg^{2+}, are incapable of changing the coordination number of the

aluminum ion in a melt compared with corundum. In addition, petrographic analysis shows that corundum partially dissolves in the melt. Hence it follows that the denominator in the relation presented above is not determined precisely.

This makes it more convenient to use the factor B to estimate the acid-base properties of calcium-containing melts [5]. Since CaO increases the basicity of melts most strongly and SiO_2 increases the acidity, the following relation was used to obtain an approximate measure of the basicity:

$$B = [CaO]/[SiO_2],$$

where [CaO] and [SiO_2] are the molar fractions of the components in the melt.

It is customary to regard melts as acidic for $B \leq 0.54$ and basic for $B \geq 2.24$. For neutral melts B falls into the intermediate range: when B increases from 0.54 to 1.30 acidity gradually changes to neutrality and from 1.30 to 2.24 to basicity.

The computed values of B for each of the modifiers are: CZAS-1 — 0.069, CZAS-2 — 0.250, and CZAS-3 — 0.440. Thus, all melts are acidic and satisfy the requirements imposed.

Considering now the effect of the viscosity of a melt on the sintering process, it should be noted that the viscosity should be minimal and it permit efficient diffusion through the liquid phase as well as crystallization of refractory phases from the liquid phase.

According to Esin and Gel'd, the interparticle interaction energy and bond strength determine the viscosity and its variation as a function of the composition [5]. Provided that the binding energy of the particles of component A is less than that of the component B, the viscosity of the liquid will

increase as the content of the component *B* increases. Since the energy of the M – O bond in the modifying oxides is lower than that of the Si – O bond, the viscosity of the melt will increase as the SiO_2 content increases, i.e., in the direction from CZAS-3 to CZAS-1.

In addition, it is known that when alkali-earth oxides are introduced into melt the decrease of the viscosity ordinarily intensifies as the radius of the ion increases. On passing from CZAS-1 to CZAS-3 the concentration of the Zn^{2+} ion, which has the smallest radius, decreases and that of the Ca^{2+} with a large radius increases; this confirms the above-indicated direction of change of the viscosity of the melt.

Finally, the investigations performed by Esin and Gel'd [5] for the three-component system $CaO – Al_2O_3 – SiO_2$ showed that the viscosity of such a melt decreases with increasing molar ratio [O] : [Si]. In our case this is observed on switching from CZAS-1 to CZAS-3 as the additive.

Therefore, with respect to the efficiency of the effect on the sintering process, taking this factor into account, the additives being considered should be arranged in the following manner: CZAS-3 → CZAS-2 → CZAS-1.

Additives with a high surface tension are the best sintering aids. In this case, corundum particles bind together effectively at an early stage of sintering.

Interchanging oxides in binary silicate melts has virtually no effect on the surface tension. But increasing alumina fraction causes the surface tension to decrease linearly. It is this character of the change in the surface tension as a function the composition of silicate melts that makes it possible to introduce the composition-independent partial surface tension $\overline{\sigma}_i$ and perform the calculation using the additivity equation

$$\sigma = \sum_i \overline{\sigma}_i x_i,$$

where x_i is the molar fraction of the component.

We determined the values of the surface tension at the melting temperature of each modifier and at an arbitrary temperature (below the complete sintering temperature).

It was found that the surface tension of melts at their melting temperatures increases in the direction from the additive CZAS-1 (392.4 mN/m) to CZAS-3 (418.0 mN/m). The modifier CZAS-2 falls in between (408.1 mN/m). At 1500°C the surface tensions are (in mN/m) 385.2 for CZAS-1, 391.6 for CZAS-2, and 408.0 for CZAS-3.

Therefore, with respect to the effectiveness of their action on the sintering process the additives studied here should be arranged in the following order: CZAS-3 → CZAS-2 → CZAS-1.

Thus, the melting temperature of the additive CZAS-1 is too high and, even though the acidity of this modifier is higher, it does not permit synthesizing a ceramic whose properties have high values. The additive CZAS-3 has the strongest effect on the sintering process. Introducing the same

amounts of this additive into compositions of the same type makes it possible to synthesize a ceramic with higher strength characteristics.

One other important fact follows from the experimental results. In all cases, for the same initial raw material the curves of the mechanical strength versus the content of the additive pass through a maximum value, equal to 4%, irrespective of the form of the additive used. Petrographic analysis shows that introducing more than 4% CZAS-2 into a composition partially destabilizes a tetragonal solid solution, and the degree of the destabilization for compositions containing 5% CZAS-2 is higher than for compositions with the amount of CZAS-3. The decomposition of a solid solution is more intense for compositions with 5% CZAS-1.

This pattern gives a basis for suggesting that SiO_2 destabilizes a tetragonal solid solution. So, a high strength remains with 4% but not 5% CZAS-2. In addition, no material containing CZAS-1, even if sintered to zero water content, showed high strength characteristics. Consequently, the amount of SiO_2 present in this ceramic can be regarded as critical. Conversion to alumina shows that the maximum amount of alumina that does not destabilize a tetragonal solid solution is 2% (molar content).

A maximum of the strength is likewise observed on the temperature curves with a constant content of the additive and initial components of the same type. However, this maximum is explained by recrystallization of aluminum oxide (more intense) and zirconium dioxide (less intense) with increasing temperature.

In summary, a dispersion-hardened material with corundum and zirconium dioxide crystals with average sizes 3 – 4 μm and 1 – 2 μm, respectively, closed porosity less than 1%, ultimate flexural strength 580 ± 40 MPa, and showing promise as a building material has been obtained on the basis of Al_2O_3-H with 4% CZAS-3 as a sintering aid and 20% PSZD added. The sintering temperature of such a ceramic is 1550°C.

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